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DETERMINATION OF GOLD IN NATURAL WATERS AT THE PARTS-PER-TRILLION (pg cm^{-3}) LEVEL

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ABSTRACT

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A combination of solvent extraction and flameless atomic absorption spectrometry was used to determine gold at the parts-per-trillion (pg cm^{-3}) level in natural waters. The method consisted of a two-step extraction procedure where Au was complexed as $HAuCl_4$ in the presence of hydrochloric acid and extracted into a small volume of methylisobutyl ketone (MIBK), where a favourable distribution ratio (D = 1250) exists. In stage *1* of the extraction, 2 l of water was acidified with 70 cm^3 of 6 *M* redistilled HCl and shaken with 55 cm^3 of redistilled MIBK. At equilibrium, the volume of solvent was reduced to ~ 5 cm^3 and extracted 76% of the Au from the water. In the second extraction stage, the MIBK extracts were further concentrated by evaporating to dryness with a rotary evaporator in the presence of ~ 5 cm^3 of the original extracted water. Standards were prepared in the same manner as the samples of natural waters. The Au was re-extracted into 0.2 cm^3 of MIBK. With a total concentration factor of ~ 10^4, coupled with the high sensitivity of flameless atomic absorption, it was possible to determine Au levels as low as 1 pg cm^{-3}. The technique was used to determine Au levels in unfiltered river-water samples draining Au-bearing Cambro-Ordovician sediments of the Meguma Group of eastern Nova Scotia, between Halifax and Sherbrooke. Au levels tended to decrease in a northeasterly direction and were highest (7 ppt) in the Little Salmon River draining Lake Major which is adjacent to the Montague Gold Mines.

INTRODUCTION

The standard procedure for determination of gold in geological materials is based on the original work of Tindall (1965) who extracted this element into methylisobutyl ketone (MIBK) from acid ($HCl—HNO_3—HBr$) solutions and then determined the Au in the organic phase by flame atomic-absorption spectrophotometry (FAA). There have been various modifications of this procedure including the work of Hall (1979) who simplified the procedure by eliminating the use of hydrobromic acid. Despite the good sensitivity of analysis of Au extracts by FAA (~ 1 $\mu g\ g^{-1}$ in the original solid sam-

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ple), the combined extraction—FAA procedure does not have sufficient sensitivity for the routine determination of Au in natural waters where levels in the range 0—100 pg cm^{-3} (ppt) are to be expected (Boyle, 1979). Brooks et al. (1967) determined trace elements at the ppb (ng cm^{-2}) level in seawater, using a combination of FAA and extraction of complexes with ammonium pyrollidine dithiocarbamate (APDC) into MIBK. Au would have been extracted under these conditions and would have given a limit of detection of ~ 1 ppb which is ~ 200 times its concentration in seawater for which Brooks (1960) determined a level of 9 ppt, using a combination of ion-exchange chromatography and emission spectrography.

The limit of detection for Au in natural waters should be lowered to ~ 10 ppt with a combination of solvent extraction and use of a heated graphite atomizer (HGA). However, this level is higher than expected Au concentrations in many natural waters. In theory, it would seem that any limit of detection could be achieved merely by increasing the volume of the aqueous phase and decreasing that of the organic phase. There are, however, practical limits to such a procedure. The relationship between the percentage extraction (E), the volume of aqueous phase (V_a), the volume of the organic phase (V_0), and the distribution ratio (D), is given by the expression:

$$E = 100D/[D + (V_a/V_0)]$$

If, for example, we have a natural water containing 10 ppt Au, and if 1 l of this water is extracted into 10 cm^3 of MIBK (where D = 100), E will be 50% and 5 ng Au will extract into the MIBK to give a solution containing 0.5 ng cm^{-3} (ppb). Decreasing the organic layer to 1 cm^3 will give a value of E of 9.1% so that 0.91 ng Au extracts and gives a concentration of 0.91 ppb. Although this procedure has nearly doubled the Au concentration in the organic layer, there are practical difficulties in recovering 1 cm^3 of solvent from a 1-l system. Moreover, this enrichment has been made at the expense of percentage recovery of the Au and the procedure may have a lower reproducibility. The problem is further compounded by the solubility of MIBK in water which is ~ 2% at 20°C (Brooks et al., 1967) and is also a funtion of the ionic strength of the aqueous phase.

We have recently developed a two-stage extraction procedure which removes the above difficulties and allows Au to be determined down to ~ 1 ppt in natural waters. The results of this investigation are reported in this paper together with data for a survey of Au in natural waters of Nova Scotia.

EXPERIMENTAL

Extractability of gold as a function of hydrochloric acid concentration

A series of 11 solutions was prepared, each with a total volume of 1 l and to which were added 0.5 μg Au (as chloride) and sufficient double-distilled constant-boiling hydrochloric acid to give final concentrations in the

range 0—0.6 *M* acid. Each solution was extracted into 25 cm^3 of redistilled MIBK after a 3-min shaking period. Because of the solubility of MIBK, the final volume of solvent was only ~ 3—4 cm^3. The organic extracts were analyzed for Au by flameless atomic absorption spectrophotometry, using a Perkin Elmer® HGA-*2200* heated graphite atomizer coupled to a Varian® AA*475* double-beam atomic absorption spectrophotometer with constant-background correction. The output was measured with a Fisher Recordall® series *100 XY* recorder. Standard operating conditions are given in Table I.

TABLE I

Standard operating conditions for the determination of Au, using flameless atomic absorption by means of a heated graphite atomizer

Argon flow rate	50 cm^3 $min.^{-1}$ with 7-s stop during atomization step
Drying step	30 s at 120°C
Charring step	30 s at 1000°C
Atomization step	7 s at 2300°C
Analysis line	242.8 nm
Lamp current	10 mA
Sample volume	20 µl
Recorder scale factor (*Y*):	5 mV $in.^{-1}$
Recorder scale factor (*X*):	100 s $in.^{-1}$

Determination of the distribution ratio of gold between hydrochloric acid solutions and MIBK

To 1 l of aqueous phase containing HCl concentrations of 6 *M*, 5 *M*, 4 *M*, 2 *M*, 1 *M*, 0.5 *M*, 0.2 *M*, and 0.06 *M*, respectively, as well as an acid-free sample, was added 50 µg Au (as chloride). This was extracted into 25 cm^3 of redistilled MIBK. The MIBK layer was removed and diluted by a factor of 10^3. Its absorbance for Au was compared with that of a similar volume of the extracted aqueous phase. The ratio of the absorbance multiplied by 10^3, gave the distribution ratio.

Development of a two-stage extraction procedure for determination of gold in waters

Stage 1. Samples of natural waters (2000 cm^3) were treated in the field with 50 cm^3 of redistilled 6 *M* HCl and shaken with 55 cm^3 of redistilled MIBK for a period of at least 5 min. The phases were allowed to settle for 1 min. and were then separated. The MIBK layer (~ 5 cm^3) was stored together with an equal volume of extracted water in a sealed polypropylene vial prior to analysis in the laboratory.

Stage 2. Samples of the previous extract were placed in turn in a 25-cm^3 pear-shaped flask attached to a Büchi Rotavapor-R® rotary evaporator and evaporated at 40°C for ~ 3 min. until the MIBK phase had disappeared. This point was indicated by a sudden effervescence. The vacuum was broken and the Au was re-extracted into 0.2 cm^3 of fresh MIBK while the flask was rotated for a further 3 min. The contents were then transferred to a 10-cm^3 measuring cylinder to facilitate removal of the organic phase which was transferred into a tiny test tube by means of a Pasteur pipette. The organic phase was analyzed for Au by HGA as soon as possible. The re-extraction procedure gave a further enrichment factor of ~ 25 compared with the first stage (400), so that the final enrichment was of the order of 10^4, and was sufficient to give a measurable signal for as little as 1 ppt in the original water sample. Samples, standards and blanks were treated in the same manner to avoid errors due to incomplete extraction during the first extraction stage.

RESULTS AND DISCUSSION

The extractability of Au as a function of HCl concentrations is shown in Fig. 1. The maximum extraction was reached in concentrations as low as 0.06 *M*. In future experiments, the acid concentration was therefore adjusted to 0.2 *M* which provided an ample safety margin for quantitative extraction while at the same time avoiding the use of an excessive amount of acid which might have produced a measurable blank.

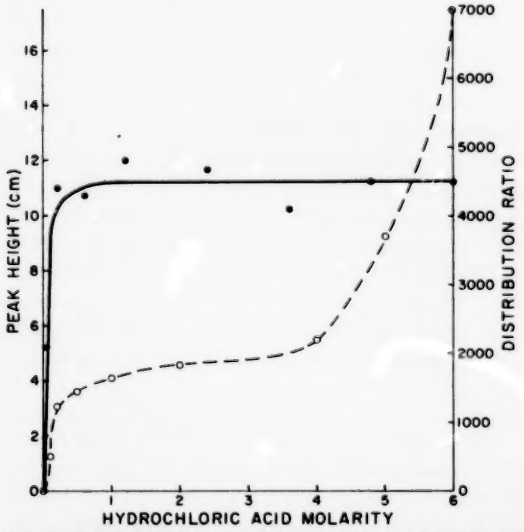

Fig. 1. Extractability of gold (recorder peak height) from hydrochloric acid into methyl-isobutyl ketone (*solid circles* and *unbroken line*) compared with values of the distribution ratio for the same system (*open circles* and *broken line*).

The distribution ratio of Au between aqueous HCl solutions and MIBK is also shown in Fig. 1. In 6 *M* acid, *D* was 7000 and decreased rapidly to 2158 in 4 *M* acid. Thereafter there was a slower decrease and the acid concentration had to be reduced below 0.2 *M* before *D* fell below 1000. In 0.2 *M* acid (the concentration used in the final procedure), *D* was 1250, under which condition, the MIBK extracted 76% of the Au during the first stage of the procedure. About 99% of this Au was re-extracted in the course of the second extraction.

In the above procedure, it is essential that standards and samples be extracted (at least for the first extraction) under the same conditions of temperature. For example, Brooks et al. (1967) showed that the solubility of MIBK in seawater is ~ 2.6% at 0°C and 1.9% at 20°C. Although this difference is only ~ 35%, very great errors are introduced if the volume of MIBK is small and if temperatures are not constant. For example, if 55 cm^3 of MIBK is added to 2000 cm^3 of seawater at 0°C, the residual volume will be 3 cm^3 whereas at 20°C the volume would have been 17 cm^3. For a given quantity of Au, the final concentration of this element would have varied by a factor of 5—6. This problem is much less serious when water samples are returned to the laboratory for analysis rather than relying on extraction in the field. In such cases, however, the water should be acidified immediately because of the risk of adsorption of Au on the walls of the container which should preferably be of polyethylene or polypropylene (Hummel, 1957).

Twelve replicate MIBK extracts of a Au solution, containing 0.5 μg in 1l of 0.2 *M* HCl, gave signals with a relative standard deviation of 5.1%. The limit of detection was ~ 1 ppt but depended on the amount of MIBK recovered during the first extraction procedure. Because of the self-compensation introduced by extracting standards in the same manner as the samples, it was not essential to recover all of the MIBK during either of the two extraction steps.

DETERMINATION OF GOLD IN NATURAL WATERS OF NOVA SCOTIA

The above analytical procedure was applied to the determination of Au in natural waters of Nova Scotia. The samples were collected in October 1980 and were extracted in the field. Samples included a seawater sample from West Arm at Halifax, two pond samples from gold mines, and 28 stream waters collected at various sites between Halifax and Sherbrooke. The locations of these samples are shown in Fig. 2. The streams all drained Au-bearing Cambro-Ordovician sediments of the Meguma Group. This formation is the site of numerous gold workings which were exploited during the 19th and early 20th centuries.

Au concentrations in all cases were lower than might have been expected, Table II. This is probably because most of the streams and rivers drained through a series of bogs and lakes so that Au might have been removed by

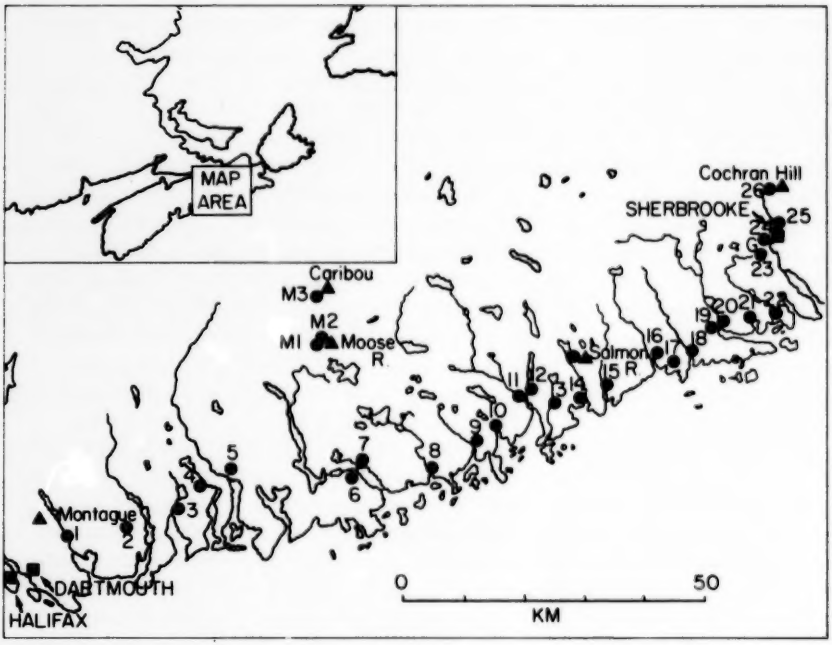

Fig. 2. Map of southeast Nova Scotia showing collection localities (*solid circles*) for water samples. Gold mines are shown as *solid triangles* designated by lower-case captions.

sedimentation or adsorption on to peat which has a strong adsorptive capacity. There was, however, a trend towards higher levels in the western part of the sampling area, particularly in the case of sample *1* which was taken from the Little Salmon River which drains Lake Major adjacent to the Montague Gold Mines, an abandoned property which was one of the largest gold producers in Nova Scotia.

In spite of the low Au levels in natural waters of Nova Scotia, the influence of some gold mines can be seen in addition to that of Montague Mines. For example, 1.7 ppt Au was found in stream waters below Moose River Mines (sample M*1*) whereas a few hundred metres upstream (sample M*2*) the level had fallen to 0.2 ppt. Although the drainage of streams through bogs and lakes renders a hydrogeochemical survey for Au of somewhat limited value, it is probable that values exceeding 5 ppt in the Meguma Group should be regarded as highly anomalous whereas background is probably below 0.5 ppt.

The value obtained for seawater is in agreement with Brooks (1960), who found 9 ppt Au, and is within the range of values (1—50 ppt Au) suggested by Boyle (1979).

TABLE II

Gold concentrations in natural waters of Nova Scotia

Sample No. (see Fig. 2)	Type of water*	Au content (pg cm^{-3} or ppt)	Sample No. (see Fig. 2)	Type of water*	Au content (pg cm^{-3} or ppt)
S	a	5	*16*	b	< 0.5
1	b	7	*17*	b	< 0.5
2	b	3	*18*	b	< 1
3	b	2	*19*	b	< 0.2
4	b	2	*20*	b	< 0.5
5	b	< 2	*21*	b	< 0.8
6	b	< 1	*22*	b	< 0.4
7	b	< 0.3	*23*	b	< 0.6
8	b	2	*24*	b	< 0.2
9	b	3	*25*	b	< 0.2
10	b	1	*26*	c	1
11	b	0.5	M*1*	b	1.7
12	b	0.6	M*2*	b	0.2
13	b	0.3	M*3*	b	< 0.1
14	b	< 0.2	G	c	0.4
15	b	< 0.5			

Variable limits of detection are due to varying recoveries of MIBK.
* a = seawater; b = stream water; c = pond water.

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